

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 3/062, 12/02, 4/20, C09D 5/00	A1	(11) International Publication Number: WO 96/33139 (43) International Publication Date: 24 October 1996 (24.10.96)
(21) International Application Number: PCT/US96/02905 (22) International Filing Date: 4 March 1996 (04.03.96) (30) Priority Data: 08/423,890 18 April 1995 (18.04.95) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor: MORRIS, Geoffrey, P.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: JORDAN, Robert, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: ACID-RESISTANT GLASS (57) Abstract An acid-resistant glass article is provided comprising: about 25-45 wt.% SiO ₂ ; about 20-35 wt.% TiO ₂ ; less than about 5 wt.% B ₂ O ₃ ; about 15-40 wt.% of an alkaline earth modifier selected from the group consisting of BaO, SrO, and mixtures thereof, and no greater than about 25 wt.% of an alkali-metal oxide selected from the group consisting of Na ₂ O, K ₂ O, and mixtures thereof. The glass article is preferably in the form of a microsphere that is adapted for use as a retroreflective element in pavement markings.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

ACID-RESISTANT GLASS

Background of the Invention

Such pavement markings typically include glass microspheres to provide retroreflective properties. However, glass microspheres embedded in the surface of painted lines and other pavement markings to serve as retroreflective elements are subjected to extremely destructive conditions. This can result from, for example, the weight of vehicles. Such conditions tend to eventually crush and/or abrade the microspheres, thereby reducing or taking away the transmission of light that is necessary for retroreflection.

Glass microspheres in pavement markings are also subject to attack by corrosive agents sometimes present in the air, such as acids formed by various emissions from automobiles, furnaces, industrial plants, etc. Such attack can cause the microspheres to become hazy and lose transparency, which also reduces or takes away their reflectivity. Conventional glass microspheres having desirable resistance to crushing, abrading, and hazing can be difficult to consistently manufacture. This is because a number of the components are volatile and tend to be released from the glass melt, thereby making it difficult to control the refractive index of the glass, for example.

Furthermore, such compositions use components, e.g., sodium fluoride, that create hazardous emissions from the glass melt, e.g., HF and SiF₄. Such components can also promote devitrification, which limits the size of glass articles that can be produced. Thus, what is needed are glass articles, particularly glass microspheres, that are acid resistant, crush resistant, and that are easier and safer to manufacture.

Summary of the Invention

The present invention provides glass articles, particularly microspheres, which combine high durability, a desirable index of refraction (e.g., about 1.6-1.9 and preferably about 1.75-1.85), and good resistance to acidic chemical agents. The term "microsphere" or "spherical" is used herein for rounded unitary glass elements used for retroreflection whether or not the elements are perfect spheres.

One aspect of the increased durability of the glass articles, e.g., microspheres is an improved crushing strength, i.e., crush resistance. As measured by a test described in the working examples, microspheres of the invention have a crush

resistance of at least about 3500 kg/cm², and preferably at least about 5000 kg/cm².

Another aspect of the increased durability is an improved acid resistance. As measured by a test described in the working examples, no more than about 20% of a set of microspheres have reduced transparency as a result of exposure to acid. That is, no more than about 20% (by number) show any visible haziness, frostiness, or opacity, as a result of 120 hours in a 1 volume-% concentrated sulfuric acid solution. Thus, as used herein, an "acid-resistant" glass composition is one that can be exposed to 1 volume-% H₂SO₄ for 120 hours with no more than about 20% of a sample of microspheres having the claimed glass composition displaying reduced transparency.

10 Preferably, the glass articles are visibly transparent (i.e., they transmit a sufficient amount of light such that they are sufficiently retroreflective for pavement marking applications) and contain no more than about 5 wt-% scattered crystallinity. The glass articles can be of any size and shape and can be used in a variety of applications. For microspheres that are suitable for use in pavement markings, they are preferably less than about 2 mm in diameter. The glass microspheres of the present invention can be used in patterned pavement marking tapes. Preferably, however, they are used in flat pavement marking tapes.

The components of the glass articles of the present invention are as follows: about 25-45 wt-% SiO₂; about 20-35 wt-% TiO₂; less than about 5 wt-% B₂O₃; about 15-40 wt-% of an alkaline earth modifier selected from the group consisting of BaO, SrO, and mixtures thereof; and no greater than about 25 wt-% of an alkali metal oxide selected from the group consisting of Na₂O, K₂O, and mixtures thereof. The ratio of the amount of SiO₂ to the total amount of alkaline earth modifier plus alkali metal oxide is greater than about 0.7. Such compositions provide acid-resistant glass. For significant acid resistance, ease of melting, and optimum refractive index (i.e., about 1.75-1.85), the glass compositions of the present invention include about 30-35 wt-% SiO₂, about 25-35 wt-% TiO₂, less than about 1 wt-% B₂O₃, about 25-35 wt-% of BaO and/or SrO, and about 4-8 wt-% of Na₂O and/or K₂O.

As is common in the glass art, the components are described as oxides, which is the form in which they are presumed to exist in the completed glass articles of the invention, and which correctly account for the chemical elements and their proportions in the composition. The starting materials used to make the glass may be some other

chemical compound than an oxide, such as barium carbonate, but the composition becomes modified to the oxide form during melting of the ingredients. Thus, the compositions of the glass articles of the present invention are discussed in terms of a theoretical oxide basis.

5 The new glass compositions of the invention are described herein in weight percent (i.e., "wt-%") of the respective components. Glass compositions are also sometimes described in mole percent (i.e., "mol-%"). Glass compositions in mole percent can be converted to weight percent as follows: (1) convert the mole percent of each oxide to mass by multiplying the molecular weight of each oxide by
10 the respective mole percent; (2) calculate the total mass for the composition; and (3) calculate the weight percent of each oxide by dividing the mass in (1) by the total mass in (2). For example, consider a glass having the following composition: 55 mol-% SiO₂; 30 mol-% BaO; and 15 mol-% TiO₂. The molecular weights for SiO₂, BaO, and TiO₂ are 60.1 g/mole, 153.3 g/mole, and 79.9 g/mole, respectively. The
15 mass of each oxide in this formulation is as follows: SiO₂ is $0.55 \times 60.1 = 33.1$ g; BaO is $0.30 \times 153.3 = 46.0$ g; and TiO₂ is $0.15 \times 79.9 = 12$ g. The glass is thus shown to comprise, in weight percents, the following: 36.3 wt-% SiO₂, 50.5 wt-% BaO, and 13.2 wt-% TiO₂.

20

Detailed Description

 The components of the glass in compositions of the invention each generally contribute different properties or degrees of a property in proportion to their amount in the composition, and combine with one another to achieve the unique properties of glass articles of the present invention. For at least the components present in
25 larger amounts, there is usually no sharp change in properties with small changes in proportions, and numerical ranges stated herein for such components should be understood in that context.

 The components and amounts of each are chosen to provide compositions having good acid resistance, good crush strength, fluidity at the melting temperature, and
30 a reasonable melting temperature (i.e., less than about 1450°C). Preferably, the components and amounts of each are also chosen to provide compositions with low volatility at the temperatures of operation (i.e., less than about 0.5 wt-% loss to

vaporization at the temperatures of operation), and low toxicity. Preferably, the glass compositions of the present invention require no fluidizing agents for improving fluidity in the melt during the manufacturing process. If fluidizing agents are used, however, they should not be volatile. Furthermore, they should not create hazardous compounds. Thus, metal fluorides are not used in the compositions of the present invention.

Silica (SiO_2) promotes glass formation and provides significant improvement in the acid-resistant characteristic of the compositions of the present invention. For the best acid resistance, at least about 25 wt-% SiO_2 is included. Too much silica, however, tends to make glass viscous and difficult to form the molten glass directly into spheres without the formation of excessive odd-shaped particles and fibers. Thus, the glass compositions of the present invention include no more than about 45 wt-% SiO_2 . For particularly advantageous results, the silica level should preferably be about 30-35 wt-%.

The index of refraction of glass elements of the invention is generally increased with increasing proportions of TiO_2 . At least about 20 wt-%, preferably about 20-35 wt-%, TiO_2 should be included to achieve the indices of refraction sought, e.g., about 1.6-1.9 and preferably about 1.75-1.85. At amounts above about 35 wt-%, the index of refraction is too high. At amounts below about 20 wt-%, the index of refraction is too low and meltability is poor. For particularly advantageous results, the TiO_2 level should preferably be about 25-35 wt-%.

An alkaline earth modifier, such as BaO or SrO (as a whole or partial substitute for BaO), is included to improve fluidity of the glass melt during formation of the glass and increases the refractive index of the glass. At least about 15 wt-%, and preferably no greater than about 40 wt-%, of BaO and/or SrO , is used in the compositions of the present invention. At amounts below about 15 wt-%, the composition is difficult to melt. At amounts above about 40 wt-% BaO , the acid resistance and crushing strength of the microspheres tends to fall below the levels sought. Thus, about 15-40 wt-% is preferably used in the compositions of the present invention, more preferably about 20-35 wt-%, and most preferably about 25-35 wt-%.

An alkali metal oxide, such as Na_2O or K_2O (as a whole or partial substitute for Na_2O), also promotes glass formation; however, too much makes the glass compositions have poor acid resistance. Greater than about 25 wt-% causes the glass

articles of the present invention to be undesirable for pavement marking. Too little alkali metal oxide results in poor melting behavior. Thus, preferably the alkali metal oxide content is about 4-25 wt-%, and more preferably about 4-8 wt-%. In preferred embodiments, the alkali metal oxide is sodium oxide, rather than potassium oxide,
5 because potassium oxide is more volatile than sodium oxide during typical glass melting operations.

Although glass compositions containing SiO_2 , TiO_2 , Na_2O and/or K_2O , and BaO and/or SrO are known, not all are acid resistant. Furthermore, not all the compositions having the amounts disclosed herein are acid resistant. Thus, the glass
10 articles of the present invention include SiO_2 , Na_2O and/or K_2O , and BaO and/or SrO in amounts such that the ratio of the amount of SiO_2 to the total amount of alkaline earth oxides (BaO and/or SrO) plus alkali metal oxides (Na_2O and/or K_2O) is greater than about 0.7, preferably greater than about 0.8. Glass compositions containing these ratios of components have good acid resistance.

15 Boria (B_2O_3) provides improvement in the level of crushing strength and promotes glass formation; however, 5 wt-% or more B_2O_3 is undesirable. This is because too much B_2O_3 can cause manufacturing problems, such as poor melting behavior and phase separation. Preferably, no more than 1 wt-% B_2O_3 is included in the glass compositions of the present invention. In particularly preferred embodiments, the glass
20 compositions are essentially free of B_2O_3 .

Another desirable component of the glass compositions of the present invention is a rare-earth metal oxide, such as La_2O_3 . Lanthanum oxide (La_2O_3), for example, promotes glass formation, aids in melting, and helps raise the refractive index while not deleteriously affecting the acid resistance or crush strength. If used, the
25 compositions of the present invention include no more than about 10 wt-% La_2O_3 , and preferably no more than about 5 wt-% La_2O_3 . If La_2O_3 is present in the compositions of the present invention, preferably no more than about 1 wt-% B_2O_3 is used. More preferably, if La_2O_3 is present, the glass compositions are essentially free of B_2O_3 .

As stated above, the glass compositions of the present invention are
30 particularly advantageous because they do not require the use of fluidizing agents. Commonly used fluidizing agents are metal fluorides (e.g. NaF , LiF , BaF_2 , KF), which can create hazardous emissions from the glass melt in the form of volatile HF and SiF_4 .

The presence of fluorine, a nonbridging anion, also promotes devitrification which limits the size of glass articles that can be prepared from the compositions of the present invention. Thus, the glass articles, e.g., microspheres, of the present invention are advantageous because they are acid resistant, they can be made in a wide variety of sizes, and they are made without metal fluoride fluidizing agents. They are also advantageous because they do not include toxic materials such as PbO.

Many other components can be included, either to contribute some specific property or to take the place of a portion of one of the other components. Generally, these other components do not total more than about 10 wt-%, preferably no more than about 5 wt-%, and more preferably no more than about 1 wt-%, of the composition (theoretical oxide basis). ZnO is an example of one possible additional component which can be added to provide meltability and fluidity to the glass melt; however, it also appears to reduce crushing strength and acid resistance. Thus, if ZnO is present, it is present in an amount of no more than about 10 wt-%, and preferably no more than about 5 wt-%. Al₂O₃ is also useful, generally in an amount of 1-5 wt-%, to contribute strength. Another useful component, although it is not desirable because of its toxicity, is As₂O₃, which can be added to make the glass elements colorless. Another component that can be included in the compositions, but is not desired, is CaO; however, this is preferably present in no more than about 5 wt-%.

Colorants can also be included in the composition of the present invention. Such colorants include, for example, CeO₂, Fe₂O₃, CoO, Cr₂O₃, NiO, CuO, MnO₂, and the like. Typically, the glass compositions of the present invention include no more than about 5 wt-%, preferably no more than about 1 wt-%, colorant, based on the total weight of the composition (theoretical oxide basis). Also, rare earth elements, such as europium, can be included for fluorescence.

The glass compositions of the present invention can also include oxides of elements that exist as impurities in certain starting materials. For example, TiO₂ can include impurities containing Al, Si, and K, which are incorporated into the glass. Typically, the glass compositions include no more than a total of about 5 wt-% of such impurities based on the total weight of the composition (theoretical oxide basis).

Glass articles of the invention can be prepared by conventional processes. In one useful process for making microspheres the starting materials are measured out in

particulate form, each starting material being preferably about 0.01 and 50 micrometers in size, and intimately mixed together. They are then melted in a gas-fired or electrical furnace until all the starting materials are in liquid form. The liquid is then quenched in water, dried, and crushed to a size desired for the final microspheres. The microsphere
5 can be screened to assure that they are in the proper range of sizes. The crushed microspheres are then passed through a flame having a temperature generally between about 1100°C and 1450°C to spheroidize the particles.

Alternatively, once the batch has been heated to the point where all starting materials are liquid, the liquid batch can be poured into a jet of high-velocity air.
10 Glass microspheres of the desired size are formed directly in the resulting stream. The velocity of the air is adjusted in this method to cause a proportion of the microspheres formed to have the desired dimensions.

Previous teachings about microspheres have noted that for the best retroreflection the microspheres should have good clarity, e.g., should contain no more than
15 5 wt-% scattered crystallinity and should be at least 95 wt-% bubble-free. However, while such a degree of clarity is preferred, it is not essential for satisfactory use of microspheres in pavement markings.

Microspheres of the invention can be incorporated into coating compositions (see, e.g., U.S. Pat. No. 3,410,185 (Harrington); U.S. Pat. No. 2,963,378
20 (Palmquist et al.); and U.S. Pat. No. 3,228,897 (Nellessen), which generally comprise a film-forming binding material in which the microspheres are dispersed. Alternatively, the microspheres can be used in drop-on applications for painted lines or incorporated into preformed retroreflective sheeting or tape. As taught, for example, in U.S. Pat. No. 2,354,018 (Heltzer et al.) or U.S. Pat. No. 3,915,771 (Gatzke et al.) tape useful for
25 pavement markings generally comprises a backing, a layer of binder material, and a layer of microspheres partially embedded in the layer of binder material. The backing can be made from various materials, e.g., polymeric films, metal foils, and fiber-based sheets.

The glass microspheres of the present invention are particularly useful in pavement-marking sheet material as described in U.S. Patent No. 4,248,932 (Tung et al.),
30 and other retroreflective assemblies, such as those disclosed in U.S. Patent Nos. 5,268,789 (Bradshaw), 5,310,278 (Kaczmarczik et al.), 5,286,682 (Jacobs et al.), and 5,227,221 (Hedblom).

Preferably, rather large microspheres, e.g., microspheres in excess of 250 micrometers in diameter, are used in "exposed-lens" pavement markings (i.e., with the microspheres partially embedded in, and partially protruding from and exposed above, the top layer of the marking) to provide the best retroreflective properties during precipitation and to minimize the effects of dirt collection. However, microspheres of the invention can be made and used in various sizes, although 200-600 micrometers is typically desired. It is difficult to deliberately form microspheres smaller than 10 micrometers in diameter, though a fraction of microspheres down to 2 or 3 micrometers in diameter is sometimes formed as a by-product of manufacturing larger microspheres. Generally, the uses for glass microspheres call for the microspheres to be less than about 2 millimeters in diameter, and most often less than about 1 millimeter in diameter.

Glass articles of the invention may be used in other shapes besides microspheres and for other purposes beside retroreflection. For example, they may be used as fibers or as flakes, and their high crush resistance and abrasion resistance adapts them to use for shot blasting or as mechanical plating media.

The invention is further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

20

EXAMPLES

Acid Resistance

Resistance to attack by acidic agents can be indicated by immersing a sample of glass microspheres in an excess of one volume percent concentrated sulfuric acid for 120 hours; then washing and drying the microspheres; and then visibly determining the percentage of microspheres that have been reduced in transparency. Different degrees of opacification are possible, from cloudy, to frosted, to separation of a thin outer shell of the microsphere from the rest of the microsphere. Microspheres that have been reduced in transparency stand out among the clear unaffected microspheres in a sample. The test is rather severe, but in a batch of microspheres of the present invention no more than about 20%, preferably no more than about 15%, and more preferably no more than about 5%, have reduced transparency.

Crush Resistance

Glass microspheres were formed and screened to sizes of about 100-200 micrometers. The crushing strength of the microspheres was measured in a bead-crushing machine, the major feature of which is two parallel plates made of very hard, non-deforming material (e.g., a ceramic, such as polycrystalline aluminum oxide). A single microsphere of known diameter was placed on the lower plate which was raised until the microsphere fails. Crushing strength is the force exerted on the microsphere at failure divided by the cross-sectional area of the microsphere (πr^2). Ten microspheres of a given composition were tested and the average result is reported as the crush resistance for the composition.

Index of Refraction

The Index of Refraction was measured by the Becke method, which is disclosed in F. Donald Bloss; "An Introduction to the Methods of Optical Crystallography"; Holt, Rinehart and Winston; New York; 47-55 (1961), the disclosure of which is incorporated herein by reference.

Example 1

1.8 Index White Beads

A glass batch was made by blending the following dry powders: 32 parts SiO_2 , 31 parts TiO_2 , 36.04 parts BaCO_3 , 10.96 parts NaNO_3 , 1.78 parts H_3BO_3 and 4 parts La_2O_3 . This mixture will yield a glass composed of 32 wt-% SiO_2 , 31 wt-% TiO_2 , 28 wt-% BaO , 4 wt-% Na_2O , 1 wt-% B_2O_3 and 4 wt-% La_2O_3 .

The raw materials were put in a platinum crucible and subsequently placed into a furnace which had been preheated to $1400^\circ \pm 50^\circ\text{C}$. The materials were observed to melt in less than about 7 minutes. The crucible was allowed to sit for a total of fifteen minutes inside the furnace at which point the crucible was removed and glass beads formed directly from the melt by pouring liquid glass directly into a stream of high velocity air (40 psi).

Glass microspheres were formed and screened to a size between 100 micrometers and 250 micrometers. These microspheres were subsequently tested for acid resistance as follows: a 0.3 g sample of beads (approximately 20,000 beads or so) was

placed inside a glass vial to which about 20-30 ml of 1-volume percent concentrated H_2SO_4 was added. The mixture was allowed to sit for five days at room temperature at which point the acid was decanted and the beads were washed several times with deionized water and then allowed to dry, at which point they were observed under a
5 microscope. For each sample, several fields of view, each containing several hundred microspheres, were examined. After this testing, the beads showed no signs of degradation or frosting (i.e., less than 5% displayed any frosting, haziness or clouding).

Crush strength was measured as described above and found to be 5065 kg/cm^2 . The index of refraction was measured as described above to be 1.82.

10

Example 2

1.8 Index Yellow Beads

The glass batch described in Example 1 was prepared with the addition of 5 parts CeO_2 . The glass was formed into beads as described above and the glass beads
15 were observed to retroreflect yellow. The beads were tested for acid resistance as described above and no frosting or degradation was observed after testing.

Example 3-15 and Comparative Examples A & B

Additional glass compositions were prepared according to the method
20 described in Example 1. The following table describes these compositions and their physical properties.

Example	SiO ₂ /(Alkali & Alkaline Earth)	SiO ₂	TiO ₂	BaO	Na ₂ O	K ₂ O	B ₂ O ₃	La ₂ O ₃	ZnO	Al ₂ O ₃	SrO	Acid Resistance (% Attacked)	Crush Strength (kg/cm ²)	Index
3	0.74	25	34	30	4	1	2	4	0	0	0	<5%		1.84-1.85
4	0.74	25	32	30	4	0	0	4	5	0	0	<5%	5925	1.84-1.85
5	0.74	28	31	30	8	0	0	3	0	0	0	<5%	5155	1.80-1.81
6	1.29	45	20	15	20	0	0	0	0	0	0	<5%	6462	1.64-1.65
7	1.00	40	20	30	10	0	0	0	0	0	0	<5%	7458	1.69-1.70
8	1.05	40	20	30	8	0	0	2	0	0	0	<5%	7618	1.80-1.81
9	0.75	30	30	37	3	0	0	0	0	0	0	15%	6395	1.80-1.81
10	1.00	32	31	0	4	0	1	4	0	0	28	<5%	6280	1.80-1.81
11	1.00	32	31	10	4	0	1	4	0	0	18	40%	7466	1.78-1.79
12	0.69	25	30	30	6	0	0	4	0	5	0	<5%	7262	1.81-1.82
13	1.00	40	20	20	20	0	0	0	0	0	0	<5%	6701	1.65-1.66
14	1.14	32	31	28	0	0	1	8	0	0	0	10%	6701	1.78-1.79
15	0.82	30	33	30	6.5	0	0	0.5	0	0	0	<5%	6863	1.81-1.82
Comparative Examples														
A	0.60	25	30	30	12	0	0	3	0	0	0	<50%		
B	0.60	25	33	25	17	0	0	0	0	0	0	>50%		

The complete disclosures of all patents, patent documents, and publications, are incorporated herein by reference as if individually incorporated. It will be appreciated by those skilled in the art that various modifications can be made to the above described embodiments of the invention without departing from the

5 essential nature thereof. The invention is intended to encompass all such modifications within the scope of the appended claims.

CLAIMS:

1. An acid-resistant glass article comprising, on a theoretical oxide basis:
 - (a) about 25-45 wt-% SiO_2 ;
 - 5 (b) about 20-35 wt-% TiO_2 ;
 - (c) less than about 5 wt-% B_2O_3 ;
 - (d) about 15-40 wt-% of an alkaline earth modifier selected from the group consisting of BaO , SrO , and mixtures thereof, and
 - (e) no greater than about 25 wt-% of an alkali metal oxide selected from the
10 group consisting of Na_2O , K_2O , and mixtures thereof;wherein the ratio of amount of SiO_2 to the total amount of alkaline earth modifier plus alkali metal oxide is greater than about 0.7.
- 15 2. The acid-resistant glass article of claim 1 further including no greater than about 10 wt-% La_2O_3 .
3. The acid-resistant glass article of claim 2 which is essentially free of B_2O_3 .
- 20 4. The acid-resistant glass article of claim 1 having an index of refraction of about 1.6-1.9.
5. The acid-resistant glass article of claim 4 having an index of refraction of about 1.75-1.85.
- 25 6. The acid-resistant glass article of claim 1 having a crush resistance of at least about 3500 kilograms per square centimeter.

7. The acid-resistant glass article of claim 1 comprising:
- (a) about 30-35 wt-% SiO_2 ;
 - (b) about 25-35 wt-% of TiO_2 ; and
 - (c) about 25-35 wt-% of the alkaline earth modifier.
- 5
8. The acid-resistant glass article of claim 1 in the form of a microsphere having a diameter of less than about 2 millimeters.
9. The acid-resistant glass article of claim 8 wherein no more than about 15% of a
- 10 sample of said microspheres have reduced transparency when exposed to 1 volume-% of concentrated H_2SO_4 for 120 hours.
10. An acid-resistant glass article comprising, on a theoretical oxide basis:
- (a) about 30-35 wt-% SiO_2 ;
 - 15 (b) about 25-35 wt-% TiO_2 ;
 - (c) less than about 1 wt-% B_2O_3 ;
 - (d) about 25-35 wt-% of an alkaline earth modifier selected from the group consisting of BaO , SrO , and mixtures thereof; and
 - (e) about 4-25 wt-% of an alkali-metal oxide selected from the group
 - 20 consisting of Na_2O , K_2O , and mixtures thereof,
- wherein the ratio of the amount of SiO_2 to the total amount of alkaline earth modifier plus alkali metal oxide is greater than about 0.7.
11. The acid-resistant glass article of claim 10 further including no greater than
- 25 about 10 wt-% La_2O_3 .
12. The acid-resistant glass article of claim 11 which is essentially free of B_2O_3 .
13. The acid-resistant glass article of claim 10 having an index of refraction of about
- 30 1.75-1.85.

14. The acid resistant glass article of claim 10 comprising about 4-8 wt-% Na_2O .
15. The acid-resistant glass article of claim 10 in the form of a microsphere having a diameter of less than about 2 millimeters.
- 5
16. A pavement marking tape comprising a backing and a layer of acid-resistant microspheres carried on the backing; wherein the acid-resistant microspheres comprise:
- 10
- (a) about 25-45 wt-% SiO_2 ;
 - (b) about 20-35 wt-% TiO_2 ;
 - (c) less than about 5 wt-% B_2O_3 ;
 - (d) about 20-40 wt-% of an alkaline earth modifier selected from the group consisting of BaO , SrO , and mixtures thereof; and
 - (e) no greater than about 25 wt-% of an alkali metal oxide selected from the
- 15
- group consisting of Na_2O , K_2O , and mixtures thereof,
- wherein the ratio of the amount of SiO_2 to the total amount of alkaline earth modifier plus alkali metal oxide is greater than about 0.7.
17. The pavement marking tape of claim 16 wherein no more than about 15% of a
- 20
- sample of said microspheres have reduced transparency when exposed to 1 volume-% of concentrated H_2SO_4 for 120 hours.
18. The pavement marking tape of claim 16 wherein the acid resistant microspheres comprise:
- 25
- (a) about 30-35 wt-% SiO_2 ;
 - (b) about 25-35 wt-% TiO_2 ;
 - (c) less than about 1 wt-% B_2O_3 ;
 - (d) about 25-35 wt-% of the alkaline earth modifier; and
 - (e) about 4-8 wt-% Na_2O .
- 30

- 19 The pavement marking tape of claim 16 wherein the acid-resistant microspheres have an index of refraction of about 1.6-1.9.
- 20 The pavement marking tape of claim 19 wherein the acid-resistant microspheres have an index of refraction of about 1.75-1.85.
- 5 21. An acid-resistant glass article consisting essentially of, on a theoretical oxide basis:
- 10 (a) 25-45 wt-% SiO_2 ;
- (b) 20-35 wt-% TiO_2 ;
- (c) less than 5 wt-% B_2O_3 ;
- (d) 20-40 wt-% of an alkaline earth modifier selected from the group consisting of BaO , SrO , and mixtures thereof;
- 15 (e) 4-25 wt-% of an alkali metal oxide selected from the group consisting of Na_2O , K_2O , and mixtures thereof, and
- (f) no greater than 10 wt-% La_2O_3 ;
- wherein the ratio of the amount of SiO_2 to the total amount of alkaline earth modifier plus alkali metal oxide is greater than about 0.7.
- 20 22. The acid-resistant glass of claim 21 consisting essentially of:
- (a) about 30-35 wt-% SiO_2 ;
- (b) about 25-35 wt-% TiO_2 ;
- (c) less than about 1 wt-% B_2O_3 ;
- (d) about 25-35 wt-% of the alkaline earth modifier;
- 25 (e) about 4-8 wt-% Na_2O ; and
- (f) no greater than about 10 wt-% La_2O_3 .

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 96/02905

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C03C3/062 C03C12/02 C03C4/20 C09D5/00

According to International Patent Classification (IPC) or in both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 946 130 (C.F.TUNG ET AL.) 23 March 1976 see column 4, line 62 - column 5, line 15; examples	1-22
X	--- CHEMICAL ABSTRACTS, vol. 106, no. 2, 12 January 1987 Columbus, Ohio, US; abstract no. 8633m, page 223; XP002007185 see abstract & JP,A,05 609 244 (NIPPON KOKAN KK ET AL.) 28 February 1981	1
X	--- US,A,4 179 300 (H. SAGARA) 18 December 1979 see the whole document --- -/-	1-15

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

1 July 1996

Date of mailing of the international search report

- 9. 07. 96

Name and mailing address of the ISA

European Patent Office, P.B. 3818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+ 31-70) 340-3016

Authorized officer

Reedijk, A

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 96/02905

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 367 919 (C.F. TUNG ET AL.) 11 January 1983 see example J -----	1,2

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No.

PCT/US 96/02905

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3946130	23-03-76	NONE	

US-A-4179300	18-12-79	JP-C- 1230816	26-09-84
		JP-A- 53092816	15-08-78
		JP-B- 59004390	30-01-84
		DE-A- 2802223	03-08-78

US-A-4367919	11-01-83	AU-B- 521101	18-03-82
		AU-B- 3847278	07-02-80
		BE-A- 869421	31-01-79
		CA-A- 1105949	28-07-81
		DE-A- 2833868	15-02-79
		FR-A,B 2399390	02-03-79
		GB-A,B 2001953	14-02-79
		JP-C- 1364937	09-02-87
		JP-A- 54034314	13-03-79
		JP-B- 61029894	10-07-86
		NL-A- 7808010	05-02-79
